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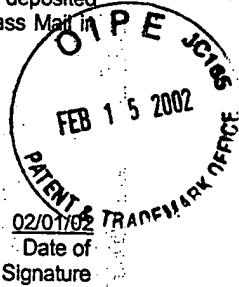
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Case #C7564(V)

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Ashcroft et al.

Serial No.: 09/940,730

Filed: August 28, 2001

For: CLEANING AID

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Sir:

Pursuant to rule 55(b) of the Rules of Practice in Patent Cases, Applicant(s) is/are submitting herewith a certified copy of the Great Britain Application No. 0021182.1 filed August 29, 2000, upon which the claim for priority under 35 U.S.C. § 119 was made in the United States.

It is respectfully requested that the priority document be made part of the file history.

Respectfully submitted,

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 UNILEVER PLC
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 LONDON EC4P 4BQ
 UNITED KINGDOM
Patents ADP number (if you know it) **1628002**

If the applicant is a corporate body, give the country/state of its incorporation

UNITED KINGDOM

4. Title of the invention

CLEANING AID

5. Name of your agent (if you have one)

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Description 24

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Abstract 1

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11. I/We request the grant of a patent on the basis of this application.

Signature *George W. Treger* Date 29.08.2000

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020 7571 6200

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C7564(V)

CLEANING AIDFIELD OF THE INVENTION

5 The present invention relates to products to assist or effect the cleaning of hard surfaces such as stainless steel, formica, perspex, ceramic or enamel.

BACKGROUND TO THE INVENTION

Household surfaces are normally cleaned using compositions which contain one or more ingredients which assist removal of fatty/oily/greasy soil and/or any visible staining such as from associated solid debris. Such compositions may be applied by pouring or as a spray, such as from a trigger spray dispenser or other aerosol applicator and rubbed with a cloth or other wipe, optionally followed by rinsing. However, it would be advantageous if the surface to be cleaned could be coated with a film of a material which would assist removal of soil and/or staining during subsequent cleaning.

We have now found that this function may be provided by an antioxidant.

JP-A-07/228,892 discloses hard surface cleansing compositions comprising anionic and amphoteric surfactants, a mono- or polyhydric alcohol and from 0.1% to 7% by weight of a tea leaf extract. Whilst tannins are commonly held to be an ingredient of tea, actually, tannic acid (an antioxidant) is actually present in very small quantities. Moreover, the role of antioxidants in assisting subsequent stain removal is not disclosed or suggested in this reference.

Other disclosures of using extracts of tea or other leaves in hard surface cleaning and/or disinfecting products are in JP-A-07/228,890 and '891, JP-A-08/104,893, JP-25 A-10/273,698, JP-A-11/100,596, JP-A-06/340,897, JP-A-62/167,400, JP-A-59/047,300 and US-A-4,220,676, although the products disclosed in the latter two contain no surfactant.

A hard surface cleaner containing from 1% to 70% by weight of anionic surfactants, 0.5% to 20% nonionic surfactants and from 0.001% to 5% by weight of tannins is disclosed in JP-A-63/196,693. An example composition comprises 15% alkylbenzene sulphonate anionic surfactant, 5% polyoxyethylene sulphate anionic surfactant, 5% coco fatty acid diethanolamide nonionic surfactant and 1% tannic acid.

5 US-A-4 094 701 discloses aqueous alkaline solutions of pH at least 9 containing a tannin and optionally, surfactant, for cleaning and etching a tin surface in the tin plate/can industry. The amounts of tannin mentioned range from 0.01 to 0.05 wt% of 10 the composition. The amount of surfactant in any such composition never exceeds 0.16 wt%.

15 US-A-5 965 514 discloses mildly acidic hard surface cleaning compositions containing amine oxide surfactant, quaternary disinfectant and a nitrogen-containing chelating agent. Optionally, a surface tension reducing agent may be included. In aqueous form, they are said to have good residue/filming properties. Tannic acid is mentioned as one of a large number of alternative possible surface tension reducing agents. It is stated that preferred members of this list can be used in amounts of from 0.005 to 2 wt%. However, tannic acid is not mentioned in this preferred list nor otherwise referred to.

20 25 Compositions for stabilising liquid or solid soap compositions for personal washing are disclosed in EP-A-0 955 355. These compositions comprise either one type or one or two different types of antioxidant, one of these being phenolic type defined by a general formula, and a surfactant. The amount of antioxidant in the compositions is given as from 0.001 to 0.1 wt% of the composition, but in the case of a liquid soap, the upper limit is given as 0.05 wt%.

An antifogging agent for glass is described in JP-A-49/113,811. This comprises by weight, 3% dialkyl sulfosuccinate anionic surfactant, 4% higher secondary alkoxyethyl sulfate anionic surfactant, 1% tannic acid, 10% propylene glycol, 5% isopropyl alcohol and 77% water.

CA-A-2 144 021 discloses microbiocidal compositions comprising short and intermediate chain fatty acids, a non-toxic phenolic compound and a solubiliser. The exemplified non-toxic phenolic compounds are compounds which are antioxidants. They are chosen for their anti-microbial properties. However, their use to promote 5 cleaning is not disclosed at all. The amount of phenolic compound before dilution of the product is from 1% to 5% by weight.

DEFINITION OF THE INVENTION

Thus, a first aspect of the present invention provides a method of removing a stain from a surface, the method comprising the steps of:-

10 (a) treating the surface with an antioxidant or with a composition comprising the antioxidant;

(b) allowing the stain to form; and

(c) cleaning the surface to remove the stain.

A second aspect of the present invention provides use of an antioxidant for 15 application to a surface to be cleaned subsequently to enable easier removal of soil and/or staining from the hard surface during said subsequent cleaning. The present invention also encompasses use of an antioxidant in the manufacture of products for use according to the second aspect of the invention.

DETAILED DESCRIPTION OF THE INVENTION

20 Whilst not being bound by any particular theory or explanation, we believe that the antioxidant exerts its effect by forming a protective film over the surface in step (a), so that stain subsequently deposited on the film in step (b) allows easier removal of the soil or stain in step (c). Therefore, a preferred form of the first aspect of the invention comprises formation of a film comprising the antioxidant, preferably by 25 drying of the antioxidant or of the composition comprising the antioxidant. Step (c) is advantageously effected using a hard surface cleaning composition comprising the antioxidant so that stain is removed and new antioxidant is applied, effectively

constituting step (a) of a subsequent process according to the first aspect of the invention. Step (c) is optionally followed by a rinsing step, preferably with water.

As used herein, the term "stain" encompasses all kinds of staining or soiling of 5 organic or inorganic origin, whether visible or invisible to the naked eye, including soiling solid debris and/or with bacteria or other pathogens.

The present invention may also deliver one or more other benefits such as improved surface feel (e.g. smoothness) during and/or after cleaning, olfactory benefits (e.g. 10 reduction in rancidity) before cleaning, less surface corrosion and less noise during cleaning. Further aspects of the present invention comprise use of an antioxidant or composition containing an oxidant, for delivery of one or more of these other benefits in a hard surface cleaning operation and/or use of the antioxidant in the manufacture of products for delivering one or more such other benefits.

15 Methods, uses, compositions and articles according to the present invention are useful for treating any household surfaces in for example kitchens and bathrooms, including cooker tops, extractor fans, tiles, floors, baths, toilets, wash hand basins, showers, dishwashers, taps, sinks, work surfaces and glass and enamel surfaces in 20 general. These surfaces may, for example, be plastics, ceramic or metal (eg. stainless steel or chrome).

The Antioxidant

As disclosed in Ingold K.V. *Adv. Chem. Ser.* 75, 296-305 (1968) "Inhibition of Autoxidation", antioxidants fall into two groups, namely primary (or chain-breaking) 25 antioxidants which react with lipid radicals to form more stable radicals, and secondary (or preventative) antioxidants which reduce the rate of chain initiation by various mechanisms. Further antioxidants may be classified as synthetic or "natural", ie. derived from natural products.

The following are classes, sub-classes and specific examples of antioxidants which 30 may be used in methods, uses, articles and compositions according to the present

invention. As used herein, the term "antioxidant" in the singular embraces one antioxidant as well as two or more antioxidant materials in combination.

A. Synthetic Antioxidants

In general, primary antioxidants are subdivided into chain-breaking acceptors and

5 chain-breaking donors.

Chain-breaking acceptors (sometimes called "preventative antioxidants") reduce oxidation rates by decomposing hydroperoxides into (non-radical) stable end products. Examples of synthetic chain-breaking acceptors include lauryl thiadipropionate, thiadipropionic acid and metal dithiocarbamates.

10 Chain-breaking donors (sometimes called "hydrogen-donating antioxidants or radical scavengers) function by competing with organic materials for peroxy radicals.

Examples of synthetic chain-breaking donors are known in the art. Examples of natural chain-breaking donors include tocopherols, ubiquinol in lipids, uric acid and ascorbic acid in serum and some of these are discussed in more detail hereinbelow.

15 Secondary antioxidants are subdivided into *inter alia* peroxide decomposers, ultra-violet absorbers, metal deactivators, (singlet oxygen) quenchers and photostabilizers.

Thermally induced homolytic decomposition of peroxides and hydroperoxides to free radicals increases the rate of oxidation. Peroxide decomposers function by decomposition to non-radical species and removes the hydroperoxides as potential

20 oxidation initiators. Most peroxide decomposers are derived from trivalent phosphorus compounds and divalent sulphur derivatives. One group of such synthetic peroxide decomposers are trivalent phosphorous compounds such as phosphites and phosphonites.

Esters of phosphorous acid derived from aliphatic alcohols and unhindered phenols

25 e.g. tris(nonylphenyl)phosphate, hydrolyse readily and have a tendency to decomposition by exposure to water or high humidity. However, their hydrolysis can be retarded by the addition of a small amount of base such as triethanolamine. Alternatively, esterified hindered phenols can be used. Relatively good resistance to

ester hydrolysis is exhibited by the hindered phenols, tris(2,4-di-tertbutylphenyl)-phosphite and tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylenediphosphonite. Bis(2,4-di-tert-butylphenyl)- pentaerythritol)diphosphate, functions as both a sterically hindered phenol and a trivalent phosphorus compound.

5 Thiosynergists are another group of synthetic peroxide decomposers. They are sulphur containing compounds which are used in conjunction with other (primary) stabilizers to enhance the effectiveness of the primary stabilizers. One commercial thiosynergist is dilaurylthiodipropionate.

10 Ultraviolet light (UV) absorbers are compounds which function by absorbing UV light and converting it to harmless energy forms. Examples of synthetic UV absorbers include benzophenones and their hydroxy- derivatives, cinnamic acid esters, phenyl salicylates, benzotriazoles and α -cyanoacrylates, amongst others.

15 Metal deactivator compounds complex with metal ions to change their redox properties mainly find application as polymer stabilizers in insulation cables. Metals having suitable oxidation-reduction potentials (e.g. Co, Cu, Fe, Mn, etc.) reduce the length of the induction period and increase the oxidation rate. Sequestrants are compounds which can bind and inactivate metal ions. For example, copper in the cables can function as a prooxidant for the adjacent polymer insulation material. Metal deactivating compounds include hindered phenolic diamides, and hindered 20 phenolic ester amides.

25 Oxamides are synthetic metal deactivator compounds which have long been known. More recently, other chemical classes, notably hydrazides, have become available commercially (optionally used in conjunction with hindered phenolics). Irganox MD 1024 and Naugard XL1 are effective as sole stabilizers as they already contain hindered phenol functionality.

30 Chelation of metal ions reduces the prooxidative effect of these ions and raises the energy of activation on the initiation reactions considerably. Chelating agents which form δ -bonds with a metal are effective as secondary antioxidants because they reduce the redox potential, thereby stabilising the oxidised form of the metal ion. Chelating agents such as heterocyclic bases which form π -complexes raise the

redox potential and accelerate oxidation, leading to pro-oxidant effects. Compounds such as citric acid (and its monoalkylesters), EDTA (ethylenediamine-tetraacetic acid), L(+)-tartaric acid (2,3,-dihydroxysuccinic acid) and phytic acid (moninositol hexaphosphoric acid) are all examples of suitable sequestrants. They exhibit
5 synergistic effects with primary antioxidants such as TBHQ, BHA, BHT, PG and tocopherols. Pyrophosphates and tripolyphosphates are most effective at forming very stable complexes with transition metal ions such as copper, iron and nickel. Phosphoric acid and its derivatives exhibit synergistic effects with BHA, BHT, and PG in fats and oils and with tocopherols in vegetable oils. Phosphonates are of
10 significant interest.

Suitable singlet oxygen quenchers include compounds such as tocopherol, DABCO (1,4-diazabicyclo[2.2.2] octane), camphor quat derivatives all exhibit good quenching properties for singlet oxygen. Polyenes such as β -carotene are also common singlet oxygen quenchers. Suitable additional compounds which show singlet oxygen
15 quenching include benzophenone 8, benzofuran and cyanurates. Quenching of singlet oxygen includes both physical and chemical quenching.

Yet other suitable synthetic antioxidants can be found from the field of photostabilizer technology. The adverse effect of light on organic materials, has been known for a long time. The major chemical compounds used commercially as UV absorbers
20 include hydroxybenzophenones, hydroxybenzotriazoles, alpha-cyanoacrylates, oxanilides and phenyl salicylates. Commercial applications of UV stabilizers include films, fibres and coatings. The activity of UV absorbers follows generally Beer-Lambert relationships i.e. an increase in absorption with increasing concentration and increasing thickness of specimens (path length). In order to achieve high levels of
25 effectiveness, relatively high concentrations of UV absorbers are used in the range of 0.25 to 4% by weight. Three kinds are especially suitable for use in the present invention.

(i) Nickel Light Stabilizers

Suitable nickel containing compounds are dibutylthiocarbamates Cryasorb 1084
30 and Irgastab 2002.

(ii) Benzoate Light Stabilizers

These materials are believed to operate via a radical trapping mechanism under photo-oxidising conditions and via hydroperoxide decomposing mechanisms by photoexcited, highly acidic phenolic hydroxyl groups, rather than photo-Fries

5 rearrangements. UV-Check AM340 is suitable since it contains both hindered and benzoate functionality.

(iii) Hindered Amine Light Stabilizers (HALS)

2,2,6,6-Tetramethylpiperidines, 2,2,6,6-tetramethyl-4-oxopiperidine-N-oxyl compounds are suitable, although the latter are strictly less preferred in view of

10 adverse colour and odour properties. Secondary hindered are usually classified as light stabilizers rather than antioxidants. Most of the commercial HALS compounds are derivatives of 2,2,6,6-tetramethylpiperidine.

B. Natural Antioxidants

Natural antioxidant compounds are particularly preferred because of their suitability

15 for use on food preparation surfaces. Any such compound may exhibit one or more of the mechanisms of antioxidation of the classes and sub-classes as hereinbefore described. However, probably most or all of them are free-radical scavengers, ie. primary antioxidants. Diverse sources of natural materials exhibiting antioxidant activity have been reported including herbs, spices, cereals, coffee and beans, oils

20 and seed, tea leaves and protein hydrolysates. The active compounds, isolated from the extracts, responsible for exhibiting antioxidant activity include, tocopherols, flavanoids, phospholipids, organic acids and their derivatives, tannins, melanoidins, terpenes, sterols, Maillard reaction products and their amino acids.

Carnosol, carnosic acid, rosmanol, rosmarinic acid, rosmarinic acid and

25 rosmarinidiphenol are known as active components of rosemary leaves which exhibit antioxidant activity. Furthermore, two major phenolic antioxidant components, gallic acid and eugenol are derived from cloves. Of the large number of compounds isolated from the extracts of herbs and spices such as sage, marjoram, oregano and thyme, some are known to have potent antioxidant and antibacterial properties.

Other natural antioxidants include β -carotene, caffeic, quinic and ferulic acid, and esters of caffeic acid with sterols (sitosterol, campesterol, gramisterol and cycloartenol). The sterol and triterpene alcohol esters of caffeic acid are not suitable. Further such compounds known to exhibit potent antioxidant activity include

5 cinnamic, sinapic, vanillic, syringic and coumaric acids.

Cardanol is a mixture of monohydroxyl phenols with a meta (3-) 15-carbon chain on the phenyl ring. It is isolated as a distillate from cashew nut shell liquid. Anacardic acid (3-n-pentadecylsalicylic acid) is the main component (80-85%) while cardanol (3-n-pentadecyl phenol) and cardol (3-n-pentadecyl resorcinol) and methyl cardanol

10 (2-methyl-5-n-pentadecyl resorcinol) are present in smaller amounts. Cardol and cardanol are commercially available. Oryzanol refers to a group of esterified sterols which have been reacted with ferulic acid (4-hydroxy-3-methoxycinnamic acid) having high molecular weight and low volatility. Sesamol, sesaminol and sesamolino compounds are constituents of sesame oil and have antioxidant

15 properties. Sesamol readily undergoes oxidation to sesamol dimer and further oxidation yields the sesamol quinone dimer.

Tocopherols and Tocotrienols

Tocopherols provide strong antioxidant activity. Like most or all natural antioxidants, tocopherols function by scavenging free radicals by their phenolic configuration, thus

20 slowing down the propagation step in the autoxidation radical sequence. Sometimes, tocopherols, under certain conditions, can form higher molecular weight materials in oils e.g. dimers, trimers, etc. Tocotrienols are a related class to the tocopherol group of compounds with the structural difference being a saturated side chain instead of an unsaturated phytol chain. The antioxidant activity of tocotrienols is less

25 than that exhibited by tocopherols due to reduced side chain conjugation resulting in fewer resonance structures. Both tocopherols and tocotrienols are known to function synergistically with ascorbic, citric, tartaric and amino acids.

Flavanoids

Some polyphenolic flavanoid compounds function as primary antioxidants, chelators and superoxide anion scavengers. These compounds function by both the "chain-

breaking" and "metal deactivating" mechanisms. The class of flavanoids is divided into subgroups of which the major members include; flavanols, flavones, isflavones, anthocyanins, catechins, proanthocyanidins and aurones. Related compounds include cinnamic and ferulic acids and their esters, some of which are precursors to

5 flavanoids. Tea leaves are a rich, inexpensive and readily available source of flavanoids (mainly catechins). When oxidized the flavanoids form polymers with complex polyphenolic structures, themselves showing antioxidant activity.

Superior to BHA and α -tocopherol as antioxidants in retarding lipid oxidation, is epigallocatechin gallate which can be extracted from tea in synergism with ascorbic

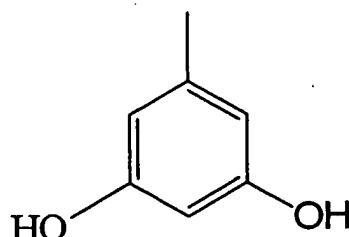
10 acid, tocopherol, citric and tartaric acids. The antioxidant activity of flavanols is related mainly to the hydroxy-group in the 3-position, the ketone at the 4-position in the pyrone ring and the double bond present at the 2,3- position. The hydroxy groups present at the 3',4' and 5, 7 or 8- positions also contribute to the antioxidant properties.

15 Rutin and chlorogenic acid also exhibit antioxidant properties, having sugar moieties attached to aromatic functionality. Compounds of this type are particularly interesting since they can partition between aqueous and organic (lipid) phases.

Tannins

Especially preferred natural antioxidants are the tannins. Tannins are a broad group

20 of plant derived phenolic compounds characterised by their ability to precipitate proteins. The phenolic groups are those which are believed to be responsible for the antioxidant activity, especially groups of formula:



or substituted derivatives thereof. Tannins and Syntans containing one or more such groups are especially preferred.

Tannic acid itself is sometimes denoted as gallotannic acid or penta-(m-digalloyl)-glucose ($C_{76}H_{52}O_{46}$). However, commercially available tannic acid is usually obtained

5 from plant and nut galls, tree barks and other plant parts and such materials are known to be gallic acid derivatives. The term "tannic acid" as used herein is to be taken to embrace all such materials.

As already mentioned, tannin-containing extracts of tea (eg. as utilised in the compositions of JP-A-07/228,892) are very low in tannic acid content. Since tannic

10 acid is a most preferred natural antioxidant in the context of the present invention, a third aspect of the present invention provides a hard surface cleaning composition comprising surfactant, more than 0.05%, preferably from 0.1% to 10% by weight of an antioxidant selected from tannic acid, a tocopherol, a tocotrienol and mixtures thereof, optionally in combination with one or more other antioxidant materials, and

15 water. Preferred types and amounts of surfactants and surfactant blends are recited elsewhere in this specification. The minimal amount of the antioxidant may be, for example, 0.1%, 0.2%, 0.25% or 0.3% by weight, eg about 0.5% and the maximum may be, for example 5%, 2.5%, 1.5% or 1% by weight.

Form of utilisation

20 The antioxidant(s) may be applied to the surface neat. However, preferably they are applied in the form of a composition containing them or by means of a wipe impregnated with the antioxidant(s) or impregnated with a composition containing the antioxidant(s).

Hard Surface Treatment Compositions

25 The antioxidant(s) can be employed according to the present invention in any suitable formulation.

The formulation must be suitable for depositing the antioxidant material onto a hard surface. The antioxidant may be present in the formulation in any suitable form, for

example in the form of a solution or dispersion. Except where expressed or implied to the contrary, they may also be in solid form, to be wetted upon use. However, in preferred embodiments, and in some aspects of the invention as a whole, they are liquids. The term "liquid" includes solutions, dispersions, emulsions, gels, pastes

5 and the like. In liquid form, they must have a pH less than 8.

Suitable liquid formulations include solutions, dispersions or emulsions of the polymeric material in a carrier, for example a substantially non-aqueous material such as ethanol, but preferably water. The compositions may be used only to deposit antioxidant, or they may have additional functions such as cleaning. In

10 general, the total antioxidant component of any such composition, may for example be from 0.01% to 10% preferably 0.1% to 1% by weight of that composition. Some preferred compositions may contain from 0.1% to 10% of antioxidant.

The composition may be applied by any suitable means. For example, it can be poured or sprayed onto the surface from a container or from an aerosol can or from a
15 spray gun applicator.

Compositions for use in the present invention may include any normal ingredients for hard surface cleaning compositions.

Preferably, a hard surface cleaning composition comprises at least one surfactant and optional other hard surface cleaning components.

20 It is especially preferred if the composition is a "liquid" having a viscosity of at least 100 centipoise (mPa.S) as measured at a shear rate of 21s^{-1} , but preferably no more than 5,000 centipoise. This viscous liquid composition may be in the form of a viscous liquid *per se*, or a gel, foam, mousse or paste. The viscosity will be due to one or more other components in the system, for example an "external structurant
25 thickener" such as CarbopolTM, or a natural polysaccharide gum such as xanthan gum or guar gum. Alternatively, an "internal structuring" system may be used, employing one or more surfactants, water, and (usually) electrolyte, to create an ordered or liquid crystalline phase within the composition. These various techniques for increasing viscosity are all very well known to those skilled in the art.

Foams and mousses are normally supplied from a dispenser which gassifies or aerates the product dispensed therefrom.

A fourth aspect of the invention comprises a liquid composition having a pH less than 8 and comprising an antioxidant, said composition having a viscosity of at least 100 5 mPaS at a shear rate of 21s^{-1} , the total amount of antioxidant in the composition being more than 0.05% by weight of the composition.

Surfactants:

A composition according to (or for use in) the invention can comprise detergent actives (surfactants) which are generally chosen from both anionic and nonionic detergent 10 actives. The composition may, for example, comprise from 0.1% to 45%, preferably from 1% to 40%, more preferably from 2% to 25% by weight of total surfactant. In many surfactant-containing compositions of the present invention, the total amount of 15 surfactant compound to be employed will generally be from 0.5 to 20%. Preferably, the amount is at least 1%, more preferably at least 3%. The maximum amount is usually 15% or less, preferably not more than 10%.

Suitable synthetic (non-soap) anionic surfactants are water-soluble salts of organic sulphuric acid esters and sulphonic acids which have in the molecular structure an alkyl group containing from 8 to 22 carbon atoms.

Examples of such anionic surfactants are water soluble salts of:

20 - (primary) long chain (e.g. 8-22 C-atom) alcohol sulphates (hereinafter referred to as PAS), especially those obtained by sulphating the fatty alcohols produced by reducing the glycerides of tallow or coconut oil;

- alkyl benzene sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;

25 - secondary alkanesulphonates;

and mixtures thereof.

Also suitable are salts of:

- alkyl glyceryl ether sulphates, especially those ethers of the fatty alcohols derived from tallow and coconut oil;
- fatty acid monoglyceride sulphates;
- 5 - sulphates of the reaction product of one mole of a fatty alcohol and from 1 to 6 moles of ethylene oxide;
- salts of alkylphenol ethyleneoxy-ether sulphates with from 1 to 8 ethyleneoxy units per molecule and in which the alkyl groups contain from 4 to 14 carbon atoms;
- the reaction product of fatty acids esterified with isethionic acid and neutralised 10 with alkali;

and mixtures thereof.

The preferred water-soluble synthetic anionic surfactants are the alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of alkyl-benzenesulphonates and mixtures with olefinsulphonates and alkyl sulphates, and the fatty acid mono-glyceride sulphates. The most preferred anionic surfactants are alkyl-aromatic sulphonates such as alkylbenzenesulphonates containing 15 from 6 to 20 carbon atoms in the alkyl group in a straight or branched chain, particular examples of which are sodium salts of alkylbenzenesulphonates or of alkyl-toluene-, -xylene- or -phenolsulphonates, alkylnaphthalene-sulphonates, ammonium 20 diamylnaphthalene-sulphonate, and sodium dinonyl-naphthalene- sulphonate.

If synthetic anionic surfactant is to be employed the amount present in the compositions of the invention, it will generally be at least 0.5%, preferably at least 1.0%, more preferably at least 2.0%, but not more than 20%, preferably at most 10%, more preferably at most 8%.

25 Although in the widest sense, soaps are not excluded from the present invention, compositions of (or for use in) the present invention are substantially free from soap, for

example containing less than 5%, preferably less than 1%, more preferably less than 0.1% by weight of soap, especially totally free of soap.

Suitable nonionic surfactants can be broadly described as compounds produced by the condensation of alkylene oxide groups, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is attached to any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired balance between hydrophilic and hydrophobic elements. This enables the choice of nonionic surfactants with the right HLB, taking into account the presence of the organic solvent and possible hydrocarbon co-solvent in the composition.

Particular examples include the condensation product of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut oil ethylene oxide condensates having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols whose alkyl group contains from 6 to 12 carbon atoms with 5 to 25 moles of ethylene oxide per mole of alkylphenol; condensates of the reaction product of ethylenediamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of ethyleneoxy groups by weight and having a molecular weight of from 5,000 to 11,000.

Other examples are: alkylglycosides which are condensation products of long chain aliphatic alcohols and saccharides; tertiary amine oxides of structure RRRNO, where one R is an alkyl group of 8 to 18 carbon atoms and the other Rs are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyldodecylamine oxide; tertiary phosphine oxides of structure RRRPO, where one R is an alkyl group of 8 to 18 carbon atoms and the other Rs are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide; and dialkyl sulphoxides of structure RRSO where one R is an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance methyltetradecyl sulphoxide; fatty acid alkylolamides; alkylene oxide condensates of fatty acid alkylolamides and alkyl mercaptans. Ethoxylated aliphatic alcohols are particularly preferred.

The amount of nonionic surfactant to be employed in the cleaning composition of the invention will preferably be at least 0.2%, more preferably at least 0.5%, most preferably at least 1%. The maximum amount is suitably 15%, preferably 10% and most preferably 7%.

- 5 The compositions may contain amounts of both anionic and nonionic surfactants which are chosen, bearing in mind the level of electrolyte present, so as to provide a structured liquid detergent composition, i.e. one which is 'self-thickened'. Thus, in spite of the presence of organic solvent, thickened liquid cleaning compositions can be made without the need to employ any additional thickening agent and which nevertheless
- 10 have a long shelf life over a wide temperature range.

The weight ratio of anionic surfactant to nonionic surfactant may vary, taking the above considerations in mind, and will depend on their nature, but is preferably in the range of from 1:9 to 9:1, more preferably from 1:4 to 4:1, and ideally above 1:1.

According to an embodiment illustrating any aspect of the invention, the compositions

- 15 may comprise from 0.1% to 7% by weight of antioxidant(s), from 0 to 20%, preferably from 0.5% to 10% by weight of a water-soluble, synthetic anionic sulphate or sulphonate surfactant salt containing an alkyl radical having from 8 to 22 carbon atoms in the molecule, and from 0.5 to 7% by weight of an ethoxylated nonionic surfactant derived from the condensation of an aliphatic alcohol having from 8 to 22 carbon atoms
- 20 in the molecule with ethylene oxide, such that the condensate has from 2 to 15 moles of ethylene oxide per mole of aliphatic alcohol, the balance being other optional ingredients and water.

It is also possible optionally to include amphoteric, cationic or zwitterionic surfactants in the compositions according to the invention.

- 25 Suitable amphoteric surfactants that optionally can be employed are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane sulphonate and sodium N-2-hydroxydodecyl-N-methyl taurate.

Suitable cationic surfactants are quaternary ammonium salts having one or two aliphatic groups of from 8 to 18 carbon atoms and two or three small aliphatic (e.g. methyl) groups, for instance cetyltrimethyl ammonium bromide.

Suitable zwitterionic surfactants that optionally can be employed are derivatives of

5 aliphatic quaternary ammonium, sulphonium and phosphonium compounds having an aliphatic group of from 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance 3-(N,N-dimethyl-N-hexadecylammonium) propane-1-sulphonate betaine, 3-(dodecyl methyl sulphonium) propane-1-sulphonate betaine and 3-(cetyl methyl phosphonium) ethane sulphonate betaine.

10 Further examples of suitable surfactants are compounds commonly used as surface-active agents given in the well-known textbooks "Surface Active Agents", Volume I by Schwartz and Perry and "Surface Active Agents and Detergents", Volume II by Schwartz, Perry and Berch.

The compositions according to the present invention may include abrasives. However,

15 these are generally not preferred as abrasives tend to damage or remove the antioxidant film being deposited on the surface. They can contain other ingredients which aid in their cleaning performance. For example, the composition can contain detergent builders such as nitrilotriacetates, polycarboxylates, citrates, dicarboxylic acids, water-soluble phosphates (especially ortho-, pyro- or polyphosphates or mixtures thereof), zeolites and mixtures thereof in an amount of up to 25%. Some of these builders can additionally function as abrasives if present in an amount in excess of their solubility in water. If present, the builder preferably will form at least 0.1% of the composition.

20 Metal ion sequestrants such as ethylenediaminetetraacetates, amino-polyphosphonates (DEQUESTTM) and phosphates and a wide variety of poly-functional organic acids and salts, can also optionally be employed provided they are compatible with the antioxidant.

25 A further optional ingredient for compositions according to the invention is a suds regulating material, which can be employed in compositions which have a tendency to produce excessive suds in use. One example of a suds regulating material is soap.

Soaps are salts of fatty acids and include alkali metal soaps such as the sodium, potassium and ammonium salts of fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 10 to about 20 carbon atoms. Particularly

- 5 useful are the sodium and potassium and mono-, di- and triethanolamine salts of the mixtures of fatty acids derived from coconut oil and ground nut oil. When employed, the amount of soap can form at least 0.005%, preferably 0.1% to 2% by weight of the composition. Fatty acid soaps such as Prifac 7901TM have been found to be suitable for this purpose.
- 10 A further example of a suds regulating material is a silicone oil. Where a hydrocarbon co-solvent is present at a sufficiently high level this may itself provide some or all of the required antifoaming activity.

Compositions according to the invention can also contain, in addition to the ingredients already mentioned, various other optional ingredients such as colourants, whiteners,

- 15 optical brighteners, soil suspending agents, deterutive enzymes, compatible bleaching agents (particularly hypohalites), gel-control agents, further freeze-thaw stabilisers, bactericides, preservatives (for example 1,2-benzisothiazolin-3-one), and hydrotropes.

Liquid (as hereinbefore defined) hard surface treatment compositions according to the invention must have a pH less than 8 but preferably they have a pH below 7,

- 20 most preferably below 5.5, especially 4.5 or less. However, it is preferred that the compositions should not be too acidic, in order to avoid damage to acid sensitive surfaces. In particular, it is important to minimise the content of sequestering organic acids which are particularly prone to attack surfaces such as enamel. Most preferably, the pH is in the region from 3 to 4.5, e.g. from 3 to 3.5.

- 25 **Liquid Dispensers**

Liquid compositions may be stored and dispensed by any suitable means but spray applicators are particularly preferred. Pump dispensers (whether spray or non-spray pumps) and pouring applicators (bottles etc) are also possible.

Thus, a fifth aspect of the present invention provides a dispenser for a liquid hard surface cleaner, the dispenser comprising a reservoir containing a liquid antioxidant or a liquid composition having a pH less than 8 and comprising an antioxidant, and spray means for dispensing acid liquid in the form of a spray.

- 5 The spray means is preferably a trigger spray but may be any mechanical means for ejecting the liquid in spray or aerosol form.

Wipes

Wipes can be impregnated with neat antioxidant(s) or with a composition containing the antioxidant(s). The material may be impregnated dry, or more preferably in wet

- 10 form (ie. as a thin or as a viscous liquid).

Suitable wipes include woven or nonwoven cloths, natural or synthetic sponges or spongy sheets, "squeegee" materials and the like.

A sixth aspect of the present invention provides a wipe impregnated with an antioxidant or a composition containing an antioxidant, such as any composition as

- 15 defined or described elsewhere in this specification.

The present invention will be described further by way of reference to the following non-limiting examples.

EXAMPLES

In the following examples, all percentages are by weight unless stated to the

- 20 contrary.

Example 1 – Kitchen Spray Composition

	Lial 111 10EO nonionic active	2%
	LAS acid anionic active	3%
	Magnesium sulphate 7H ₂ O	0.9%
5	Sodium hydroxide	0.57% (to pH 5.5)
	Radimix dicarboxylic acids	0.4%
	Proxel GXL preservative	0.016%
	Perfume	0.35%
	Sodium cumene sulphonate hydrotrope	1%
10	Propylene glycol t-butyl ether solvent	2%

Example 2 – Kitchen Spray Composition

As Example 1 but with the tannic acid replaced by 0.25% ascorbyl palmitate plus 0.25% alpha tocopherol.

15

Control 1

As Example 1 but without tannic acid.

Example 3 – Gel Composition

20	2% Lial 111-5EO Nonionic surfactant
	5% Lial 111-10EO Nonionic surfactant
	0.5% tannic acid (Tanex ALsok)
	0.1% citric acid
	0.10% Dequest 2010 sequestrant
25	0.2% Keltrol RD
	0.08% Proxel – preservative
	balance water
	pH adjusted to 4.5 with sodium hydroxide
	Viscosity: 130cps (21s ⁻¹) 32cps (106s ⁻¹)

30

Control 2

As Example 3 but without tannic acid.

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Example 4 – Impregnated Wipe

The following liquid composition was prepared.

5 2.88% isopropyl alcohol
2.16% butyl digol
0.134% benzalkonium chloride
0.36% nonionic surfactant C11 10 Eo
10 0.5% tannic acid
0.2% sodium hydroxide
0.144% perfume
0.05% sodium EDTA
balance water

15 Wipes in the form of non-woven 70% viscose/30% polyester cloths were stacked in a wipe dispensing box and impregnated by pouring-in the liquid composition.

Evaluation

20

Substrate Details

A stainless steel substrate was used for cleaning tests. This was brushed stainless steel size 380mm by 300mm (grade 304 sheet BS 1449 Pt2 1983, supplied by Merseyside Metal Services Ltd). This size tile accommodates two areas for cleaning, 25 one on the left and one on the right of the tile. Each area for cleaning is 215mm by 150mm.

Pre-cleaning of Stainless Tiles

The tiles were pre-cleaned prior to a cleaning experiment as follows:

30

- ◆ commercial liquid abrasive cleaner (Jif Cream cleaner), cleaning with a damp J-cloth and rinsed with hot water;

- ◆ liquid dish-washing detergent (Persil Dishwashing Liquid), cleaning with a damp J-cloth and rinsed with hot water;
- ◆ calcite, cleaning with a damp J-cloth and rinsed hot water, and finally rinsed with demineralised water;

5 ◆ after allowing the tiles to drain-dry, they are wiped with a paper towel, ensuring all calcite deposits are removed.

Application of Pre-treatment to Stainless Steel Tiles

10

A cardboard mount revealing the two areas of the tile to be pre-treated was placed onto the stainless steel tile. To one of the 215mm x 150mm areas, approximately half of a 1.0ml pipetted aliquot was applied in a line across the top 150mm section of the pre-treatment area. The remaining portion of the 1.0ml prototype kitchen product

15

was similarly applied to the lower 150mm section of the area. The cardboard mount was carefully removed from the steel tile in readiness to wipe the applied prototype over the entire pre-treatment area. A dampened hand-wrung J-clothTM

(demineralised water) was folded around a 150mm plastic ruler. This was used to spread the 1.0ml aliquot of the composition being tested, over the steel surface. The

20

prototype was spread using four linear wipes over the designated area, two downward and two upward wipes, and in each case 4 replicates for cleaning were prepared. After pre-treatment application, the tiles were allowed to dry for 2 hours before spraying with dehydrated castor oil soil.

25

Soiling and Ageing the Pre-treated Stainless Steel Tiles

The spraying of the castor oil soil was carried out in a fume cupboard under standard conditions to ensure good reproducibility between different experiments. The soil was dehydrated castor oil with 0.2% fat red 7B dye. This was stored in the

30

refrigerator when not in use. It was equilibrated to ambient temperature before spraying.

The fume cupboard walls/floor and the lab-jack were covered with paper towel. A lab-jack was used to elevate the tile to a practical height for spraying. The lab-jack height was 200mm and was positioned centrally at the back of the fume cupboard. A

5 line 40mm from the back wall of the fume cupboard was marked on to the top of the lab-jack, this was used as the positioning line for each steel tile before spraying. From the 40mm line on the lab-jack, a line 270mm, in parallel, was marked on the base of the fume cupboard floor. This was where the perspex spray guide was aligned when spraying.

10

A commercially available gravity fill spray gun was used to spray the oily soil onto the steel tile. The rear dial on the gravity fill gun was rotated 360° anti-clockwise from the closed position and the side dial was rotated 270° anti-clockwise, again from the closed position. The gravity fill spray gun was attached to a floor standing air

15 compressor unit and a pressure of 25p.s.i. was used for spraying this soil on to the steel tiles. A clamp stand was positioned in the fume cupboard to hold the spray gun when not in use. The dehydrated castor oil soil was poured into the open bowl of the spray gun.

20 The cardboard spray mount was clipped to a stainless steel tile and this was centrally placed, in landscape position, on the lab-jack along the 40mm line from the rear of the fume cupboard. The cardboard spray mount was a rectangular piece of card, the same size as a stainless steel tile, with two cut-out areas sized 215mm by 150mm, one window area on the left side and the other to the right, with a card separator border between the two windows. The perspex spray guide was positioned in front of the first window of the tile to be sprayed directly on the 270mm line. This area of the tile was sprayed for a total of 35 seconds starting from the top, following the line of the spray guide. The time taken to spray from top to bottom was approximately 9 seconds, therefore the track of the spray guide is traced 4 times, for each 215mm by 150mm area being sprayed. After spraying the first area of the tile, the adjacent area was sprayed in exactly the same way, after re-aligning the perspex spray guide in front of the second area. Once the entire tile had been sprayed twice, it was removed from the fume cupboard and the cardboard spray mount carefully removed.

The sprayed tiles were stacked directly on to an oven shelf, each stainless steel tile being separated using an aluminum ring spacer placed in each corner. These spacers enabled each tile to be separated by 10mm. When all the tiles were sprayed, they were collectively placed in the oven for ageing.

5

The tiles were aged at a temperature of 85°C for 1.5 hours. The prepared tiles were not cleaned until the next day.

10 The effort used to remove the soil from the test surface using a cellulosic spongeweb was measured.

Formulations tested were the compositions of Example 1; Example 2 and the control corresponding to Example 1 minus the tannic acid.

15 Results given are geometric means of the 4 replicate experiments.

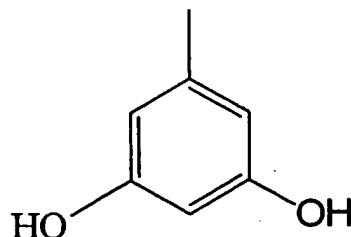
Treatment	Average Log 10 Effort	Average Total Effort (Ns)
No treatment (not totally clean in 2 minutes)	3.798	6337
Control 1	3.212	1639
Example 1	1.998	109
Example 2	2.868	791

20

Treatment	Average Log 10 Effort	Average Total Effort (Ns)
No treatment	3.713	5171
Control 2	3.177	1507
Example 3	1.96	92

CLAIMS

1. A method of removing a stain from a surface, the method comprising the steps in sequence, of:-
 - 5 (a) treating the surface with an antioxidant or with a composition comprising the antioxidant;
 - (b) allowing the stain to form; and
 - (c) cleaning the surface to remove the stain.
2. Use of an antioxidant in the manufacture of a product containing that antioxidant, the product being for application to a surface to be subsequently cleaned to enable easier removal of soil and/or staining from the hard surface during said subsequent cleaning.
- 10 3. A process according to claim 1 or use according to claim 2, wherein said antioxidant comprises a primary antioxidant.
- 15 4. A process or use according to any preceding claim, wherein said antioxidant comprises a natural antioxidant.
5. A process or use according to any preceding claim, wherein said antioxidant comprises a tannin.
- 20 6. A process or use according to any preceding claim, wherein the antioxidant comprises a compound having one or more optionally substituted groups of formula



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7. A process or use according to any preceding claim, wherein the antioxidant is selected from tannic acid, a tocopherol, a tocotrienol and mixtures thereof, optionally in combination with one or more other antioxidant materials.
8. A process or use according to any preceding claim, wherein said antioxidant
5 is applied in the form of a liquid composition having a pH less than 8 and viscosity of at least 100 mPaS at a shear rate of 21s^{-1} .
9. A process or use according to any preceding claim, wherein said composition further comprises a surfactant and water.
10. A process or use according to claim 9, wherein said composition comprises
10 from 0% to 20%, preferably from 0.5% to 10% by weight of synthetic anionic surfactant.
11. A process or use according to claim 9 or claim 10, wherein said composition comprises from 0.2% to 15% by weight of nonionic surfactant.
12. A process or use according to any of claims 1-7, wherein the antioxidant is
15 applied as a wipe impregnated with the antioxidant or with a composition comprising the antioxidant.
13. A process or use according to claim 12, wherein the composition is a composition as defined in any of claims 8-11.
14. A liquid composition having a pH less than 8 and comprising an antioxidant
20 and having a viscosity of at least 100 mPaS at a shear rate of 21s^{-1} .
15. A composition according to claim 14, comprising a thickener.
16. A composition according to claim 14, wherein the viscosity is due to one or more surfactants and optionally, electrolyte, in said composition.
17. A composition according to any of claims 14-16, being a composition as
25 defined in any of claims 9-11.

18. A composition according to any of claims 14-17, wherein the antioxidant is as defined in any of claims 3-7.
19. A liquid hard surface cleaning composition having a pH less than 8 and comprising surfactant, more than 0.05%, preferably from 0.1% to 10% by weight of an antioxidant selected from tannic acid a tocopherol, a tocotrienol and mixtures thereof, optionally in combination with one or more other antioxidant material, and water.
5
20. A dispenser for a liquid hard surface cleaner, the dispenser comprising a reservoir containing a liquid antioxidant or a liquid composition having a pH less than 8 and comprising an antioxidant, and spray means for dispensing said liquid in the form of a spray.
10
21. A dispenser according to claim 20, wherein the spray means is a trigger spray.
22. A dispenser according to claim 20 or claim 21 wherein the liquid in the reservoir is a liquid composition according to any of claims 14-19.
15
23. A dispenser according to any of claims 20-22, wherein the antioxidant is as defined in any of claims 3-7.
24. A wipe impregnated with an antioxidant or with a composition comprising an antioxidant.
20
25. A wipe according to claim 24, impregnated with a composition according to any of claims 14-19.
20
26. A wipe according to claim 24 or 25, wherein the antioxidant is as defined in any of claims 3-7.
25

ABSTRACT

CLEANING AID

A method of removing a stain from a surface, comprises the steps of:-

5 (a) treating the surface with an antioxidant or with a composition comprising the antioxidant;

 (b) allowing the stain to form; and

 (c) cleaning the surface to remove the stain